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<p>(54) Title: METHODS AND DEVICES FOR CONTROLLING THE OXIDATION RATE OF A HYDROCARBON BY ADJUSTING THE RATIO OF THE HYDROCARBON TO A RATE-MODULATOR</p> <p>(57) Abstract</p> <p>Methods and devices for controlling the oxidation rate of a hydrocarbon to an acid by adjusting addition of a rate-modulator are disclosed. In order to control oxidation rate, the ratio of hydrocarbon to rate-modulator is appropriately adjusted. Preferably, this ratio is adjusted continually based on feedback relative to oxidation progress parameters. It may be kept substantially constant at steady state conditions of the oxidation, or it may take a path of predetermined values. The rate-modulator preferably comprises a hydrocarbon oxidation initiator.</p>			

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METHODS AND DEVICES FOR CONTROLLING THE OXIDATION RATE OF A HYDROCARBON BY ADJUSTING THE RATIO OF THE HYDROCARBON TO A RATE-MODULATOR

TECHNICAL FIELD

5 This invention relates to methods of making dibasic acids, such as adipic acid for example, by oxidizing a hydrocarbon, such as cyclohexane for example, with a gas containing an oxidant, preferably oxygen.

BACKGROUND ART

There is a plethora of references (both patents and literature articles) 10 dealing with the formation of acids, one of the most important being adipic acid, by oxidation of hydrocarbons. Adipic acid is used to produce Nylon 66 fibers and resins, polyesters, polyurethanes, and miscellaneous other compounds.

15 There are different processes of manufacturing adipic acid. The conventional process involves a first step of oxidizing cyclohexane with oxygen to a mixture of cyclohexanone and cyclohexanol (KA mixture), and then oxidation of the KA mixture with nitric acid to adipic acid. Other processes include, among others, the "Hydroperoxide Process", the "Boric Acid Process", and the "Direct Synthesis Process", which involves direct oxidation of cyclohexane to adipic acid with oxygen in the presence of solvents, catalysts, and initiators or promoters.

20 The Direct Synthesis Process has been given attention for a long time. However, to this date it has found little commercial success. One of the reasons is that although it looks very simple at first glance, it is extremely complex in reality. Due to this complexity, one can find strikingly conflicting results, comments, and views in different references.

25 It is important to note that most studies on the Direct Oxidation have been conducted in a batch mode, literally or for all practical purposes.

There is a plethora of references dealing with oxidation of organic compounds to produce acids, such as, for example, adipic acid and/or intermediate products, such as for example cyclohexanone, cyclohexanol, cyclohexylhydroperoxide, 30 etc.

The following references, among the plethora of others, may be considered as representative of oxidation processes relative to the preparation of diacids and intermediate products.

- U.S. Patent 5,463,119 (Kollar), U.S. Patent 5,374,767 (Drinkard et al), U.S. Patent 5,321,157 (Kollar), U.S. Patent 3,987,100 (Barnette et al.), U.S. Patent 3,957,876 (Rapoport et al.), U.S. Patent 3,932,513 (Russell), U.S. Patent 3,530,185 (Pugi), U.S. Patent 3,515,751 (Oberster et al), U.S. Patent 3,361,806 (Lidov et al), U.S. Patent 3,234,271 (Barker et al), U.S. Patent 3,231,608 (Kollar), U.S. Patent 3,161,603 (Leyshon et al), U.S. Patent 2,565,087 (Porter et al), U.S. Patent 2,557,282 (Hamblet et al), U.S. Patent 2,439,513 (Hamblet et al), U.S. Patent 2,223,494 (Loder et al), U.S. Patent 2,223,493 (Loder et al), German Patent DE 44 26 132 A1 (Kysela et al), and PCT International Publication WO 96/03365 (Constantini et al).
- None of the above references, or any other references known to the inventors disclose, suggest or imply, singly or in combination, oxidation reactions to intermediate oxidation products under conditions subject to the intricate and critical controls and requirements of the instant invention as described and claimed.

Our U.S. Patents 5,580,531, 5,558,842, 5,502,245, as well as our PCT International Publication WO 96/40610 describe methods and apparatuses relative to controlling reactions in atomized liquids.

DISCLOSURE OF THE INVENTION

- As aforementioned, this invention relates to methods of making dibasic acids by oxidizing a hydrocarbon with a gas containing an oxidant, preferably oxygen.
- More particularly, it relates to a method of controlling oxidation rate of a C5-C12 cycloaliphatic hydrocarbon to the corresponding dibasic acid, comprising the steps of:
- (a) feeding continually into a reaction zone an oxidant and a rate-modulator in the presence of a catalyst and a solvent, under conditions causing oxidation of the hydrocarbon to the dibasic acid by the oxidant, the hydrocarbon and the rate-modulator being fed at a first ratio, the solvent comprising an organic acid containing only primary and/or secondary hydrogen atoms; and
- (b) adjusting said first ratio in a manner that the oxidation rate falls within a range of desired values.

The oxidation rate is the amount of hydrocarbon oxidized to organic products, excluding carbon monoxide and dioxide, per unit time.

The first ratio may be adjusted continually based on feedback relative to oxidation progress parameters, or it may be kept substantially constant at steady state conditions of the oxidation, or it may take a path of predetermined values.

It is preferable that the rate-modulator comprises a hydrocarbon oxidation initiator. It is more preferable that the rate-modulator is selected from a

group consisting of an aldehyde corresponding to the organic acid of the solvent, a ketone corresponding to the cycloaliphatic hydrocarbon, a peroxide, and a mixture thereof. It is even more preferable that the rate-modulator is selected from a group consisting of an aldehyde corresponding to the organic acid of the solvent, a ketone corresponding to the cycloaliphatic hydrocarbon, and a mixture thereof. It is further even more preferable that the rate-modulator comprises a ketone corresponding to the cycloaliphatic hydrocarbon.

It is also preferable that the rate-modulator comprises cyclohexanone, the aliphatic hydrocarbon comprises cyclohexane, the solvent comprises acetic acid, the oxidant comprises oxygen, and the catalyst comprises cobalt species.

The oxidation rate may be determined by a step of monitoring oxidant depletion in the reaction zone and/or pressure variations in the reaction zone and/or gas flow differentials between gases entering and gases exiting the reaction zone, or by other ways.

The method of this invention may also comprise a step of premixing the rate-modulator with at least one of solvent, catalyst, and hydrocarbon to form a first mixture, and then feeding said first mixture into the reaction zone. Further, the method may comprise a step of atomizing the first mixture in the reaction zone.

The present invention also pertains to a method of controlling the oxidation rate of cyclohexane to adipic acid, comprising the steps of:

- (a) partially oxidizing cyclohexane to a second mixture comprising cyclohexanone, the second mixture having a desired second ratio of cyclohexane to cyclohexanone;
- (b) feeding the mixture into a reaction zone in the presence of a catalyst, a solvent and an oxidant, and under conditions causing formation of adipic acid;
- (c) adjusting said desired second ratio in a manner that the oxidation rate falls within a desired range.

This method may further comprise a step of feeding additional cyclohexane or cyclohexanone to the reaction zone for modifying said desired second ratio.

The second ratio may be adjusted continually based on feedback relative to oxidation progress parameters, or it may be kept substantially constant at steady state conditions of the oxidation, or it may take a path of predetermined values. Further, the ratio may be adjusted continually based on feedback relative to oxidation progress parameters, or it may be kept substantially constant at steady state conditions of the oxidation, or it may take a path of predetermined values.

As in the previous case, the oxidation rate may be determined for example by a step of monitoring oxidant depletion in the major reaction zone and/or pressure variations in the major reaction zone and/or gas flow differentials between gases entering and gases exiting the major reaction zone. Also, this method may further 5 comprise a step of atomizing the second mixture in the major reaction zone.

The desired range of the second ratio preferably falls between 99.5/0.5 and 95/10. However, this also depends on whether cyclohexane or cyclohexanone or a combination of cyclohexane and cyclohexanone are also fed directly to the major reaction zone. Under such circumstances the above mentioned preferable limits of 10 99.5/0.5 and 95/10, are adjusted accordingly to take into account such additional feeding.

It is extremely important to continually control the ratio of hydrocarbon to rate-modulator, such as for example an oxidation initiator like cyclohexanone for example, not only in order to control the oxidation rate, but also to ensure that the 15 selectivity and/or yield to the desired oxidation product, such adipic acid for example does not suffer.

It was found unexpectedly by the inventors that in certain ranges of hydrocarbon to rate-modulator ratios, the selectivity starts suffering considerably, although the oxidation rate increases. For example, in the case that the hydrocarbon is 20 cyclohexane, the rate-modulator is cyclohexanone, and the desired oxidation product is adipic acid, ratios of hydrocarbon to rate-modulator lower than 80/20 deteriorate the selectivity considerably. Thus, it is of utmost importance that the modulation of the oxidation rate is limited to ranges at which the selectivity is not deteriorated excessively. A balance of reaction rate and selectivity may be determined in each 25 particular case and the appropriate range of hydrocarbon to rate-modulator be employed.

The oxidation may take place in a preceding reaction zone and in the major reaction zone, the preceding reaction zone being at a higher temperature than the major reaction zone.

30 The instant invention, also encompasses a device for controlling the oxidation rate of a C5-C12 cycloaliphatic hydrocarbon to the corresponding dibasic acid, comprising:

a major reaction chamber;
first feeding means for feeding into the major reaction chamber the 35 cycloaliphatic hydrocarbon;

second feeding means for feeding continually into the major reaction chamber an oxidation rate-modulator;

third feeding means for feeding into the major reaction chamber an oxidant;

5 fourth feeding means for feeding into the major reaction chamber a catalyst and a solvent, the solvent comprising an organic acid containing only primary and/or secondary hydrogen atoms;

condition controlling means for controlling conditions in the major reaction chamber in a manner to induce oxidation of the hydrocarbon by the oxidant;

ratio adjusting means for causing the hydrocarbon and the rate-modulator to be fed into the major reaction chamber at a first ratio, and optionally adjusting said first ratio in a manner that the oxidation rate falls within a range of desired values.

- 10 This device may further comprise feedback means connected to the major reaction chamber, and the ratio adjusting means may be adapted to adjust the first ratio continually based on feedback from the feedback means, the feedback being relative to oxidation progress parameters.

- 15 The feedback preferably comprises means for monitoring oxygen depletion during the oxidation and/or pressure variations in the major reaction chamber and/or gas flow differentials between gases entering and gases exiting the major reaction chamber.

20 The ratio adjusting means may be adapted to maintain the first ratio substantially constant at steady state conditions of the oxidation, or to guide the first ratio through a path of predetermined values, among other variations.

- 25 Further, the device of the present invention may comprise premixing means for premixing the rate-modulator with at least one of solvent, catalyst, and hydrocarbon to form a first mixture, and then feeding said first mixture into the major reaction chamber. Preferably the device may also comprise atomizing means for atomizing the first mixture in the major reaction chamber.

- 30 A different embodiment of the present invention involves a device for controlling the oxidation rate of cyclohexane to adipic acid, comprising in combination an assembly of:

35 a precursory reaction chamber;

first cyclohexane feeding means for feeding cyclohexane into the precursory reaction chamber;

- 35 first oxidant feeding means for feeding an oxygen containing gas into the precursory reaction chamber in order to partially oxidize the cyclohexane to a

second mixture comprising cyclohexanone, the second mixture having a desired
second ratio of cyclohexane to cyclohexanone;
a major reaction chamber;
second mixture feeding means for feeding the second mixture into the major
reaction chamber;
5 additional feeding means for feeding one or more of a catalyst, a solvent and an
oxidant into the major reaction chamber;
condition controlling means for controlling conditions in the major reaction
chamber in a manner to induce oxidation of the hydrocarbon by the oxidant;
10 and
ratio adjusting means for adjusting said second ratio in a manner that the
oxidation rate falls within a range of desired values.

This device may further comprise a second cyclohexane feeding means
for feeding cyclohexane to the major reaction chamber for modifying said desired
15 second ratio.

It is further preferable that the device further comprises feedback means
connected to the major reaction chamber, and wherein the ratio adjusting means are
adapted to adjust the second and/or ratio continually based on feedback from the
feedback means, the feedback being relative to oxidation progress parameters in the
20 major reaction chamber. More preferably, the feedback means are adapted to monitor
oxygen depletion during the oxidation and/or pressure variations in the major reaction
chamber and/or gas flow differentials between gases entering and gases exiting the
major reaction chamber.

The ratio adjusting means may be adapted to maintain the second ratio
25 substantially constant at steady state conditions of the oxidation, or to guide the second
ratio through a path of predetermined values.

The device may further comprise premixing means for premixing the
second mixture with at least one of solvent, catalyst, cyclohexane, and cyclohexanone
to form a third mixture, and then feeding said third mixture into the major reaction
30 chamber. The device preferably further comprises atomizing means for atomizing the
third mixture in the major reaction chamber.

Further, this invention pertains to a device for controlling the oxidation
rate of a C5-C12 cycloaliphatic hydrocarbon to the corresponding dibasic acid,
comprising:

35 a preceding reaction chamber;

first feeding means for feeding into the preceding reaction chamber the cycloaliphatic hydrocarbon;

second feeding means for feeding continually into the preceding reaction chamber a oxidation rate-modulator;

5 third feeding means for feeding into the preceding reaction chamber an oxidant;

fourth feeding means for feeding into the preceding reaction chamber a catalyst and a solvent, the solvent comprising an organic acid containing only primary and/or secondary hydrogen atoms;

10 a major reaction chamber connected to the preceding reaction chamber in a manner that contents of the preceding reaction chamber may move to the major reaction chamber;

means for maintaining the temperature of the preceding reaction chamber higher than the temperature of the major reaction chamber; and

15 ratio adjusting means for causing the hydrocarbon and the rate-modulator to be fed to the preceding reaction chamber at a first ratio, and optionally adjusting said first ratio in a manner that the oxidation rate in the major reaction chamber falls within a range of desired values.

The lower conversions per stage, according to this invention, simplify the heat transfer problems as well as the design of each reaction chamber. Furthermore, 20 they provide better energy efficiency.

BRIEF DESCRIPTION OF THE DRAWINGS

The reader's understanding of this invention will be enhanced by reference to the following detailed description taken in combination with the drawing figures, wherein:

25 Figure 1 illustrates schematically a preferred embodiment of the present invention comprising a major reaction chamber 12.

Figure 2 illustrates schematically a different preferred embodiment of the present invention, wherein a precursory reaction chamber 11 is utilized, in addition to the major reaction chamber 12, for forming a mixture of hydrocarbon and rate-30 modulator having a desirable ratio.

Figure 3 illustrates schematically a still different preferred embodiment of the present invention, wherein a preceding reaction chamber 9 is utilized, in addition to the major reaction chamber 12, operated at a higher temperature than the major reaction chamber 12.

BEST MODE OF CARRYING OUT THE INVENTION

As mentioned earlier, this invention relates to methods of making intermediate oxidation products, such as acids, for example, by oxidizing a hydrocarbon with a gas containing an oxidant, preferably oxygen.

For purposes of clarity and brevity, the most preferred constituents may be used to exemplify the methods of the present invention, instead of more generic terms. For example "acetic acid" may be used instead of "solvent," but it should be understood that any other suitable solvent(s) may be used in said methods. Examples of less preferred solvents are butyric acid, propionic acid, etc. In a similar manner, "acetaldehyde" or "cyclohexanone" may be used instead of the more generic name "initiator" or "promoter," and "cobalt acetate tetrahydrate," or "cobalt acetate" (both meaning "cobaltous acetate tetrahydrate" unless otherwise specified) may often be used instead of the more generic term "catalyst."

In addition to the formation of adipic acid, the methods of the present invention may also be applied to other diacids from the corresponding cyclic aliphatic hydrocarbons. Examples are formation of glutaric acid from cyclopentane, formation of pimelic acid from cycloheptane, and the like.

As aforementioned, initiators have been used so far to initiate a reaction, such as oxidation of cyclohexane to adipic acid, for example. This initiation of reaction or oxidation shortens an induction period considerably. The induction period in their absence is in most occasions unacceptably long, frequently of the order of days, while in their presence, the induction period is rather short, frequently of the order of a fraction of one hour. The explanation accepted by many researchers is that the initiators induce oxidation of the catalyst, which usually comprises cobaltous ions, to cobaltic ions. Cobaltic ions are necessary in the mechanism of oxidations, such as the oxidation of cyclohexane to adipic acid for example. After a certain amount of cobaltic ions have been formed, the mechanisms proposed involve a combination of cobaltous and cobaltic ions, both of which are considered as being regenerated through formation of intermediate species during the oxidation. Initiators in the production of cyclic alcohols or ketones may be added to the reactants at the start or continuously during the oxidation or both.

It was found unexpectedly by the inventors that initiators may beneficially be used continually to control the rate of oxidation, and that they may be used as oxidation rate-modulators. Oxidation rate-modulators are defined, according to the instant invention, as compounds, the continual addition of which in a reaction zone

or a reaction chamber may change controllably the rate of oxidation, in a manner that the oxidation rate attains a value within a desired or predetermined range of values.

Compounds which may be used as oxidation rate-modulators, or simply rate-modulators, include but are not limited to oxidation initiators, such as for example, acetaldehyde, cyclohexanone, methylethylketone, etc.

It is extremely important to continually control the ratio of hydrocarbon to rate-modulator, such as for example an oxidation initiator like cyclohexanone for example, not only in order to control the oxidation rate, but also to ensure that the selectivity and/or yield to the desired oxidation product, such adipic acid for example does not suffer.

It was found unexpectedly by the inventors that in certain ranges of hydrocarbon to rate-modulator ratios, the selectivity starts suffering considerably, although the oxidation rate increases. For example, in the case that the hydrocarbon is cyclohexane, the rate-modulator is cyclohexanone, and the desired oxidation product is adipic acid, ratios of hydrocarbon to rate-modulator lower than 80/20 deteriorate the selectivity considerably. Thus, it is of utmost importance that the modulation of the oxidation rate is limited to ranges at which the selectivity is not deteriorated excessively. A balance of reaction rate and selectivity may be determined in each particular case and the appropriate range of hydrocarbon to rate-modulator be employed.

In such oxidations, a solvent is involved, such as acetic acid for example. If an aldehyde is used as a rate-modulator, it is preferable that the aldehyde corresponds to the acid used as solvent in the oxidation reaction. If acetic acid is the solvent used in the oxidation, for example, acetaldehyde should preferably be used as a rate-modulator. Similarly, if an aldehyde is to be used in an oxidation as a rate-modulator, and if the solvent is propionic acid, the aldehyde corresponding to propionic acid should be preferably utilized. The use of acetic acid as solvent is highly preferred, because it is considerably more stable than other organic acids. Use of the corresponding aldehyde is preferable because if oxidized it turns to the corresponding acid. Thus, if acetaldehyde is used as a rate-modulator, and if it is oxidized it turns to acetic acid which is the solvent.

In a similar manner, if a ketone is used as the rate-modulator, it is preferable that the ketone corresponds to the hydrocarbon which is to be oxidized. Thus, in the case that the hydrocarbon to be oxidized to adipic acid is cyclohexane, the preferable ketone to be used as a rate-modulator should be cyclohexanone. Use of cyclohexanone as a rate-modulator, in the case of direct synthesis of adipic acid, is of

particular interest because cyclohexane may initially be partially oxidized to form just a small appropriate amount of cyclohexanone, and then further oxidized to adipic acid.

Control of the oxidation rate is of utmost importance. A delicate balance between yield and oxidation rate exists, depending on the particular circumstances. If 5 the oxidation rate is unacceptably high, low yields may be observed, and even explosions may occur. On the other hand, if the oxidation rate is too low, the production rate is also too low, and even with 100% yield the process may be grossly uneconomical. This delicate balance may be easily determined for any particular circumstances, and optimized. What is important is to be able to control the oxidation 10 rate within a desired range, depending on the particular circumstances.

A preferred embodiment of this invention is illustrated in Figure 1. In Figure 1, there is depicted a device or continuous reactor system 10 comprising a major reaction chamber 12, which includes a major reaction zone 34.

Connected to the major reaction chamber 12 are a hydrocarbon feeding 15 line 50i; a solvent feeding line 52i; a catalyst feeding line 54i; a rate-modulator (which may be an initiator or promoter) feeding line 56i; a gaseous oxidant feeding line 18; a gas outlet line 17; a predominantly non-gas outlet line 21; a recycle feeding line 14; a pressure monitor 68; a temperature monitor 22; and an optional oxygen monitor or analyzer 25, which samples preferably the vapor contents of the major reaction chamber 20 12 through orifice 23.

The gas outlet 17 is also connected to a gas outlet assembly 71 which may comprise a controllable assembly of condenser(s) for removing condensable matter, valve(s), flowmeter(s) and the like (not shown for purposes of clarity), similar to the ones described in our aforementioned co-pending applications and/or issued patents. 25 The gas inlet 18 is also connected to a gas inlet assembly 73, which may comprise a controllable assembly of valve(s), flowmeter(s) and the like for providing a gaseous oxidant to the major reaction chamber, and it may be similar to the ones described in our aforementioned co-pending applications and/or issued patents. Both the inlet assembly 73 and the outlet assembly 71 are controlled and also give flow rate feedback 30 data to a controller 28, which is preferably a computerized controller.

The controller 28 also controls a number of valves 50, 52, 54, and 56 through output lines 50", 52", 54", and 56", respectively, which valves in turn regulate the flow of ingredients through inlet lines 50i, 52i, 54i, and 56i, respectively.

The thermocouple or temperature monitor 22, the pressure monitor 68, 35 and the oxygen monitor 25 give information to the controller 28 regarding temperature,

pressure and oxygen content respectively. The oxygen analyzer may be any well known to the art oxygen analyzer.

A flowmeter in each of the inlet lines 50i, 52i, 54i, and 56i, is not shown in Figure 1 for purposes of clarity. Their purpose is to give flow information to the controller 28, useful for the regulation of valves 50, 52, 54, and 56 so that they deliver a desired flow for each ingredient.

Lines 50i, 52i, 54i, and 56i, may be heated by well known to the art techniques, or as described in our co-pending applications, and/or patents, individually or collectively or otherwise. These lines may also merge, if so desired, and their contents premixed before entering the major reaction chamber 12.

The major reaction chamber 12 may be a stirred tank reactor, a recirculation reactor, an atomization reactor, or other type of reactor known to the art.

Monitors (not shown) for carbon monoxide, carbon dioxide, oxygen, and/or other gases may also be placed preferably in one of the of gas lines 17 or 19.

In operation of this embodiment, hydrocarbon, cyclohexane for example, solvent, acetic acid for example, catalyst, cobalt acetate tetrahydrate for example, preferably in the form of a solution comprising solvent for example, and a rate-modulator, such as an oxidation initiator or promoter, like cyclohexanone or acetaldehyde, for example enter the major reaction chamber 12 as disclosed in our co-pending applications, and/or patents. At the same time that the aforementioned ingredients enter the major reaction chamber 12, a gaseous oxidant also enters through line 18, and starts reacting with the hydrocarbon. No recyclables exist at the initial stages.

After the reaction has been initiated a certain flow of predominantly non-gaseous matter is initiated through line 21, which matter contains products of oxidation, by-products, and unreacted ingredients. The flow is arranged so that a desired conversion of hydrocarbon to acid, depending on the particular circumstances, but usually between 5% and 50%, has been attained. In the case of atomization reactors, the ingredients, including recyclables, are preferably premixed before entering the major reaction chamber 12. The products may be separated products from by-products and recyclables at a further stage, similar to the stages disclosed in our co-pending applications and/or patents. The recyclables may enter the major reaction chamber 12 through inlet line 14. Of course, line 14 may be merged with one or more of lines 50i, 52i, 54i, and 56i, before a mixture of the respective ingredients enters the major reaction chamber 12.

The temperature in the major reaction chamber 12 is monitored by one or more thermocouples or temperature monitors 22, and the controller adjusts the heat flow to or from the major reaction chamber in a manner that a temperature within a desired range is maintained. The heat flow may be controlled either through heaters 5 (not shown) on the individual lines 50i, 52i, 54i, 56i, and 14, or directly by heating or cooling the major reaction chamber 12 itself, or by other methods well known to the art.

The controller, based on information regarding oxygen consumption, which is representative of oxidation rate, especially after correction for carbon monoxide and carbon dioxide formation, adjusts the ratio of hydrocarbon to rate-modulator entering the major reaction chamber 12 so that the reaction or oxidation rate 10 is maintained within desired limits. The adjustment is predominantly made by regulating 50 and 56 after taking into account the composition of the recyclables.

If the rate of oxidation is too high, the controller 28 changes the settings of valves 50 and 56 so that the ratio of hydrocarbon to rate-modulator is increased. 15 Similarly, if the rate of oxidation is too low, the controller 28 changes the settings of valves 50 and 56 so that the ratio of hydrocarbon to rate-modulator is decreased.

If the reaction has reached steady conditions of oxidation, meaning that among other parameters the rate of oxidation attains a substantially constant value, and if this value remains within the desired range, the hydrocarbon to rate-modulator ratio 20 may remain also substantially constant.

Further, it may be preferable, under certain circumstances, that the hydrocarbon to rate-modulator ratio takes a path of predetermined values in a manner that the desirable range of values of the rate of oxidation follows also a desired path. For example, especially in the case of a batch or semi-batch reactor, it may be desirable 25 that at the beginning a low ratio is employed, which becomes higher toward the end of the reaction, for achieving better yield for example.

In the case that the hydrocarbon is cyclohexane and the rate-modulator is cyclohexanone, an initial ratio of 97 to 3 is preferable. As the oxidation proceeds, the ratio may preferably be varied in the range of 99.9 / 0.1 to 80 / 20, and more preferably 30 in the range of 99 / 1 to 90 / 10. Ratios lower than 80/20 usually produce large amounts of undesired by-products, while ratios higher than 99.9 / 0.1 are ineffective.

Changes and adjustments in the ratio of hydrocarbon to rate-modulator are preferably made in frequency of time increments ranging from 1/5 to 1/50 of the hold-up time of the contents of the major reaction chamber 12 in the case of stirred tank 35 reactors. The controller 28 may control the timing, frequency and magnitude of such changes and adjustments, depending on the dynamics of the system, according to a

desired program. If the feedback to the controller shows large effects with an adjustment, the frequency of a next adjustment is preferably decreased and/or the magnitude of the adjustment is also decreased. Similarly, if the feedback to the controller shows small effects with an adjustment, the frequency of a next adjustment is 5 preferably increased and/or the magnitude of the adjustment is also increased. Hold up time is the time that it would take for a reaction chamber to be emptied at the flow rate of line 21, with nothing being added to the reaction chamber.

The oxidation rate may be calculated by the controller by measuring the oxidant, preferably oxygen, entering through line 18, the oxidant leaving through line 10 17, and formation of carbon monoxide and carbon dioxide. The oxidation rate may also be determined by measuring the pressure drop rate at different time intervals. The oxidation rate may further be calculated by measuring the consumption of oxidant, by means of monitor 25, after the entering and exiting of oxidant is stopped for short periods of time. One measurement of oxidant may be taken at the beginning of such 15 period, and one at the end of the period. The difference, shows the consumption of oxidant at this period of time. The oxidant monitor may be positioned on line 17 or 19, and the content of oxidant monitored. From the difference of this content and the amount of oxidant entering the major reaction chamber, the controller calculates the rate of oxidant consumption and the oxidation rate from the oxidant consumption rate. In all 20 cases, the amounts of carbon dioxide and carbon monoxide formed are preferably monitored and taken into account for the oxidation rate calculation by the controller, unless these amounts of carbon dioxide and carbon monoxide are either too small or constant for all practical purposes. Well known to the art chromatographic techniques 25 may also be employed to determine the oxidation rate form the consumption of hydrocarbon per unit time.

In another preferred embodiment of the instant invention, better shown in Figure 2, there is provided a precursory reaction chamber 11, which includes a precursory reaction zone 34a. A number of feeding inlet lines, line 80 for hydrocarbon, line 81 for initiator and line 82 for catalyst are connected to the precursory reaction 30 chamber 11. Line 83 is for oxidant introduction, preferably oxygen or oxygen containing gas, and line 84 is for allowing off-gases to exit the precursory reaction chamber 11. The products of reaction are moved from the precursory reaction chamber 11 to the major reaction chamber 12 through line 85. The reaction parameters, such as flows, temperatures, pressure, etc., of the precursory reaction chamber 11 are controlled 35 by the controller 28 through a multiple output line 11" by well known to the art techniques.

Auxiliary inlet lines (such as lines 50i, 54i, and 56i, for example, as shown in Figure 1) may also be present for additional control of the final composition entering the major reaction chamber 12.

- In operation of this embodiment, cyclohexane, initiator, such as for example cyclohexanone or acetaldehyde, and catalyst, such as for example cobalt salt, preferably in the absence of acidic solvent, are added to the precursory reaction chamber 11 through lines 80, 81, and 82, respectively. A gaseous oxidant, preferably comprising oxygen, enters the precursory reaction chamber through inlet line 83, and the off gases exit through outlet line 84. The product of oxidation, comprising cyclohexane and cyclohexanone, having a second ratio of cyclohexane to cyclohexanone, is fed to the major reaction chamber 12 for further oxidation to adipic acid. A solvent, such as acetic acid for example is also added to the major reaction chamber 12 through line 52i. The controller 28, as aforementioned, receives information related to oxidation rate in the major reaction chamber 12 through one or more of input lines 68', 22', 23', 71' and 73'.
- If the oxidation rate in the major reaction chamber 12 is higher than a desired range, the controller 28 changes the operational parameters of the precursory reaction chamber 11, in a manner to decrease the second ratio of cyclohexane to cyclohexanone in inlet line 85, until the oxidation rate in the major reaction chamber 12 falls within the desired range. Similarly, if the oxidation rate in the major reaction chamber 12 is lower than a desired range, the controller 28 changes the operational parameters of the precursory reaction chamber 11, in a manner to increase the second ratio of cyclohexane to cyclohexanone in inlet line 85, until the oxidation rate in the major reaction chamber 12 falls within the desired range. The desired range of the second ratio preferably falls between 99.5/0.5 and 95/10. However, this also depends on whether cyclohexane or cyclohexanone or a combination of cyclohexane and cyclohexanone are also fed directly to the major reaction chamber 12. Under such circumstances the above mentioned preferable limits of 99.5/0.5 and 95/10, are adjusted accordingly to take into account such additional feeding.

- For example, increase of temperature, and/or increase of the initiator level, and/or the catalyst level entering the precursory reaction chamber 11, as ordered by the controller 28, decrease the second ratio of cyclohexane to cyclohexanone. A decrease in these operational parameters, among others, as ordered by the controller 28 through multiple output line 1", has an opposite result. Also an increase in hold-up time in the precursory chamber 11, results in a decreased cyclohexane to cyclohexanone second ratio. A decrease in hold-up time in the precursory chamber 11, results to an increased cyclohexane to cyclohexanone second ratio.

It is preferable that the oxidation in the precursory reaction chamber 11 takes place in the absence of solvent, while the oxidation in the major reaction chamber 12 takes place in the presence of a solvent, such as acetic acid for example.

Additional inlet lines (not shown) may introduce to the major reaction 5 chamber more cyclohexane and/or cyclohexanone so that the second ratio is modified in a manner to bring the oxidation rate within a desirable range.

In still a different preferred embodiment of the instant invention, better shown in Figure 3, there is provided a preceding reaction chamber 9, which includes a preceding reaction zone 34b. The preceding reaction chamber 9 is fed by lines 50i, 52i, 10 54i, 56i, and 14 (recyclables after reaction in major reaction chamber 12), either directly or after a pre-mixing chamber (not shown) and/or after a heat exchanger (not shown). A gaseous oxidant, preferably comprising oxygen, enters the preceding reaction chamber 9 through inlet line 86, and the off gases exit through outlet line 87. Line 88 connects the preceding reaction chamber 9 with the major reaction chamber 12 for moving matter 15 from the preceding reaction chamber 9 to the major reaction chamber 12. The preceding reaction chamber 9 is connected (not shown for purposes of clarity) with the controller 28 through input and output lines, similar to the input and output lines connecting the controller 28 with the major reaction chamber 12.

In operation of this embodiment, the oxidation temperature in the 20 preceding reaction chamber 9 and the preceding reaction zone 34b is set by the controller higher than the temperature in the major reaction chamber 12. Recyclables enter the preceding reaction chamber 9, as well as one or more of hydrocarbon, solvent, catalyst and rate-modulator, through lines 50i, 52i, 54i, 56i, respectively, in amounts regulated by valves 50, 52, 54, and 56, respectively, which valves are in turn regulated 25 by the controller 28 through output lines 50", 52", 54", and 56", respectively. The conversion of cyclohexane to adipic acid in the preceding reaction chamber 9, as measured in line 88, is preferably low, preferably in the range of 0.01% to 5%, more preferably in the range of 0.1% to 3%, and even more preferably in the order of 0.5 % to 1%. The rest of the conversion, as measured in line 21, is preferably less than 80%, and 30 more preferably less than 40%. However conversions in other ranges are not excluded.

The controller, based on information regarding oxygen consumption in the major reaction chamber 12, which is representative of oxidation rate, especially after correction for carbon monoxide and carbon dioxide formation, adjusts the ratio of hydrocarbon to rate-modulator entering the preceding reaction chamber 9 so that the 35 reaction or oxidation rate in the major reaction chamber 12 is maintained within desired

limits. The adjustment is predominantly made by regulating valves 50 and 56 after taking into account the composition of the recyclables.

- If the rate of oxidation is too high, the controller 28 changes the settings of valves 50 and 56 so that the ratio of hydrocarbon to rate-modulator is increased.
- 5 Similarly, if the rate of oxidation is too low, the controller 28 changes the settings of valves 50 and 56 so that the ratio of hydrocarbon to rate-modulator is decreased.

In the case that the hydrocarbon is cyclohexane and the rate-modulator is cyclohexanone, an initial ratio of 97 to 3 is preferable. As the oxidation proceeds, the ratio may preferably be varied in the range of 99.9 / 0.1 to 80 / 20, and more preferably 10 in the range of 99 / 1 to 90 / 10. Ratios lower than 80/20 usually produce large amounts of undesired by-products, while ratios higher than 99.9 / 0.1 are ineffective.

Changes and adjustments in the ratio of hydrocarbon to rate-modulator are preferably made in frequency of time increments ranging from 1/5 to 1/50 of the hold-up time of the contents of the major reaction chamber 12 in the case of stirred tank reactors. The controller 28 may control the timing, frequency and magnitude of such changes and adjustments, depending on the dynamics of the system, according to a desired program. If the feedback to the controller shows large effects with an adjustment, the frequency of a next adjustment is preferably decreased and/or the magnitude of the adjustment is also decreased. Similarly, if the feedback to the 15 controller shows small effects with an adjustment, the frequency of a next adjustment is preferably increased and/or the magnitude of the adjustment is also increased.

A dual reaction chamber, as described above is useful in achieving higher output without sacrificing yield excessively.

Oxidations according to this invention, are non-destructive oxidations, 25 wherein the oxidation product is different than carbon monoxide, carbon dioxide, and a mixture thereof. Of course, small amounts of these compounds may be formed along with the oxidation product, which may be one product or a mixture of products.

Examples include, but of course, are not limited to preparation of C₅ - C₁₂ aliphatic dibasic acids from the corresponding saturated cycloaliphatic 30 hydrocarbons, such as for example preparation of adipic acid from cyclohexane.

Regarding adipic acid, the preparation of which is especially suited to the methods and apparatuses of this invention, general information may be found in a plethora of U.S. Patents, among other references. These, include, but are not limited to:

U.S. Patents 2,223,493; 2,589,648; 2,285,914; 3,231,608; 3,234,271; 35 3,361,806; 3,390,174; 3,530,185; 3,649,685; 3,657,334; 3,957,876; 3,987,100;

4,032,569; 4,105,856; 4,158,739 (glutaric acid); 4,263,453; 4,331,608; 4,606,863;
4,902,827; 5,221,800; and 5,321,157.

Examples demonstrating the operation of the instant invention have been given for illustration purposes only, and should not be construed as limiting the scope of this invention in any way. In addition it should be stressed that the preferred embodiments discussed in detail hereinabove, as well as any other embodiments encompassed within the limits of the instant invention, may be practiced individually, or in any combination thereof, according to common sense and/or expert opinion. Individual sections of the embodiments may also be practiced individually or in combination with other individual sections of embodiments or embodiments in their totality, according to the present invention. These combinations also lie within the realm of the present invention. Furthermore, any attempted explanations in the discussion are only speculative and are not intended to narrow the limits of this invention.

All explanations given hereinabove are to be considered as speculative and should not be construed as limiting the breadth of the claims.

CLAIMS

What is claimed is:

1. A method of controlling the oxidation rate of a C5-C12 cycloaliphatic hydrocarbon to the corresponding dibasic acid, comprising the steps of:

(a) feeding continually into a major reaction zone an oxidant and a rate-modulator in the presence of a catalyst and a solvent, under conditions causing oxidation of the hydrocarbon to the dibasic acid by the oxidant, the hydrocarbon and the rate-modulator being fed at a first ratio, the solvent comprising an organic acid containing only primary and/or secondary hydrogen atoms; and

(b) adjusting said first ratio in a manner that the oxidation rate falls within a range of desired values.

2. A method as defined in claim 1, wherein the rate-modulator has been formed at least partially by partially oxidizing the cycloaliphatic hydrocarbon to a second mixture comprising the rate-modulator, the second mixture having a second desired ratio of hydrocarbon to rate-modulator.

3. A method as defined in claim 2, wherein the first ratio is adjusted at least partially by adjusting the second ratio.

4. A method as defined in claim 1, 2, or 3, wherein the first ratio and/or the second ratio are/is adjusted by a step of feeding additional hydrocarbon and/or rate-modulator to the major reaction zone.

5. A method as defined in claim 1, 2, 3, or 4 wherein the first ratio and/or the second ratio are/is adjusted continually based on feedback relative to oxidation progress parameters.

6. A method as defined in claim 1, 2, 3, 4, or 5, wherein the first ratio and/or the second ratio are/is substantially constant at steady state conditions of the oxidation.

7. A method as defined in claim 1, 2, 3, or 4, wherein the first ratio and/or the second ratio take(s) a path of predetermined values.

8. A method as defined in claim 1, 2, 3, 4, 5, 6, or 7, wherein the oxidation rate is determined by a step of monitoring oxidant depletion in the major reaction zone and/or pressure variations in the major reaction zone and/or gas flow differentials between gases entering and gases exiting the major reaction zone.

9. A method as defined in claim 1, 2, 3, 4, 5, 6, 7, or 8, further comprising a step of atomizing the first mixture in the major reaction zone.

10. A method as described in claim 1, 2, 3, 4, 5, 6, 7, 8, or 9, wherein the oxidation takes place in a preceding reaction zone and the major reaction zone, the preceding reaction zone being at a higher temperature than the major reaction zone.

11. A method as defined in claim 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10, wherein the rate-modulator is selected from a group consisting of an aldehyde corresponding to the organic acid of the solvent, a ketone corresponding to the cycloaliphatic hydrocarbon, a peroxide, and a mixture thereof.

12. A method as defined in claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, or 11, wherein the rate-modulator comprises cyclohexanone, the aliphatic hydrocarbon comprises cyclohexane, the solvent comprises acetic acid, the oxidant comprises oxygen, the catalyst comprises cobalt species, and the dibasic acid comprises adipic acid.

13. A device for controlling the oxidation rate of a C5-C12 cycloaliphatic hydrocarbon to the corresponding dibasic acid, comprising:

a major reaction chamber;

first feeding means for feeding into the major reaction chamber the cycloaliphatic hydrocarbon;

second feeding means for feeding continually into the major reaction chamber a oxidation rate-modulator;

third feeding means for feeding into the major reaction chamber an oxidant;

fourth feeding means for feeding into the major reaction chamber a catalyst and a solvent, the solvent comprising an organic acid containing only primary and/or secondary hydrogen atoms;

condition controlling means for controlling conditions in the major reaction chamber in a manner to induce oxidation of the hydrocarbon by the oxidant;

ratio adjusting means for causing the hydrocarbon and the rate-modulator to be fed at a first ratio, and optionally adjusting said first ratio in a manner that the oxidation rate falls within a range of desired values.

14. A device as defined in claim 13, further comprising feedback means connected to the major reaction chamber, and wherein the ratio adjusting means are adapted to adjust the first ratio continually based on feedback from the feedback means, the feedback being relative to oxidation progress parameters.

15. A device as defined in claim 14, wherein the feedback comprises monitoring oxygen depletion during the oxidation and/or pressure variations in the major reaction chamber and/or gas flow differentials between gases entering and gases exiting the major reaction chamber.

16. A device as defined in claim 13, 14, or 15, wherein the ratio adjusting means are adapted to maintain the first ratio substantially constant at steady state conditions of the oxidation.

17. A device as defined in claim 13, 14, or 15, wherein the ratio adjusting means are adapted to guide the first ratio through a path of predetermined values.

18. A device as defined in claim 13, 14, 15, 16, or 17, further comprising atomizing means for atomizing the first mixture in the major reaction chamber.

19. A device as defined in claim 13, 14, 15, 16, 17, or 18, further comprising:

a precursory reaction chamber;
first hydrocarbon feeding means for feeding hydrocarbon into the precursory reaction chamber;

first oxidant feeding means for feeding an oxygen containing gas into the precursory reaction chamber in order to partially oxidize the hydrocarbon to a second mixture comprising the oxidation rate-modulator, the second mixture having a desired second ratio of hydrocarbon to oxidation rate-modulator; and

second mixture feeding means for feeding the second mixture into the major reaction chamber.

20. A device as defined in claim 19, further comprising means for maintaining the temperature of the preceding reaction chamber higher than the temperature of the major reaction chamber.

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FIG. 1

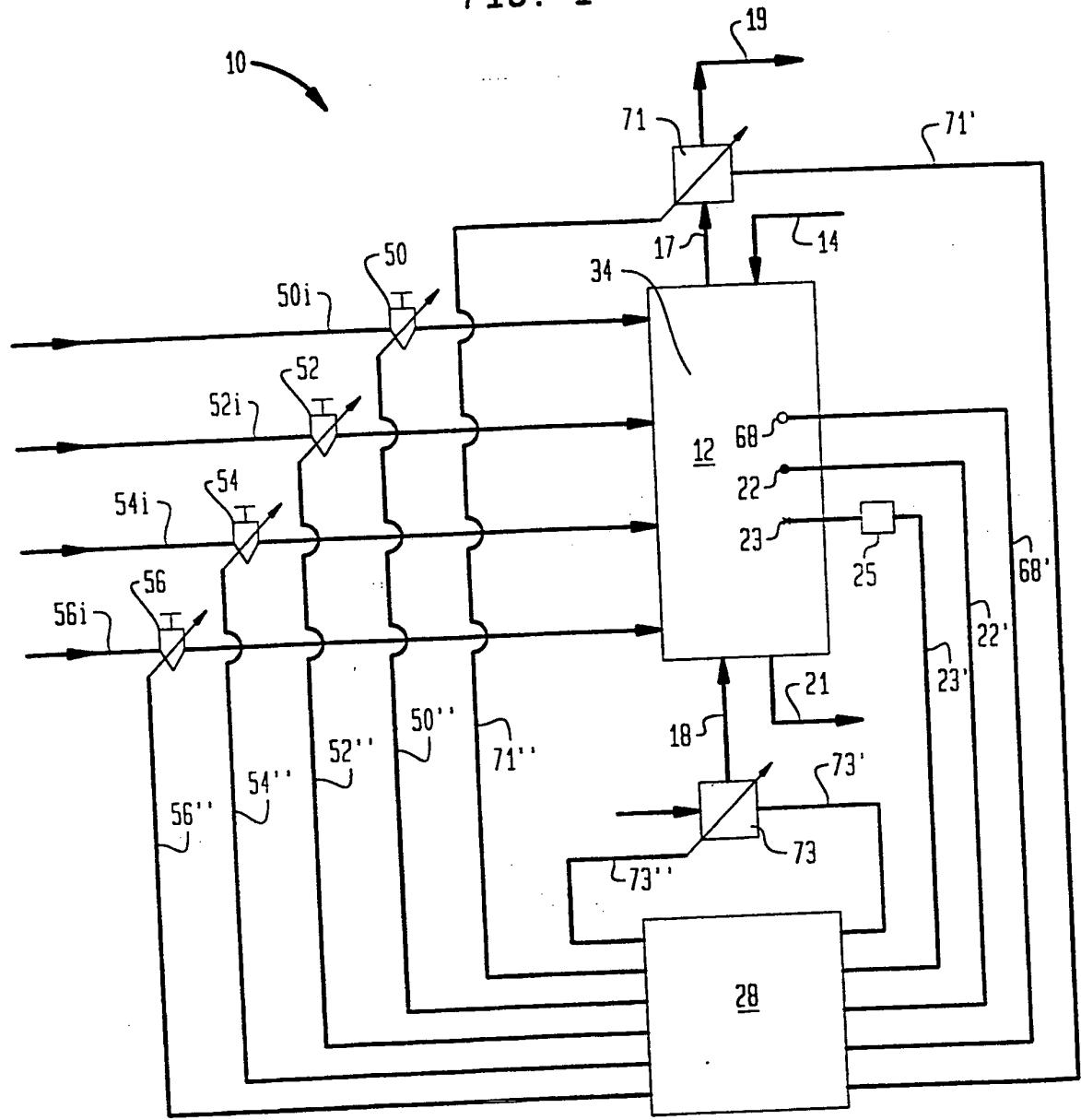
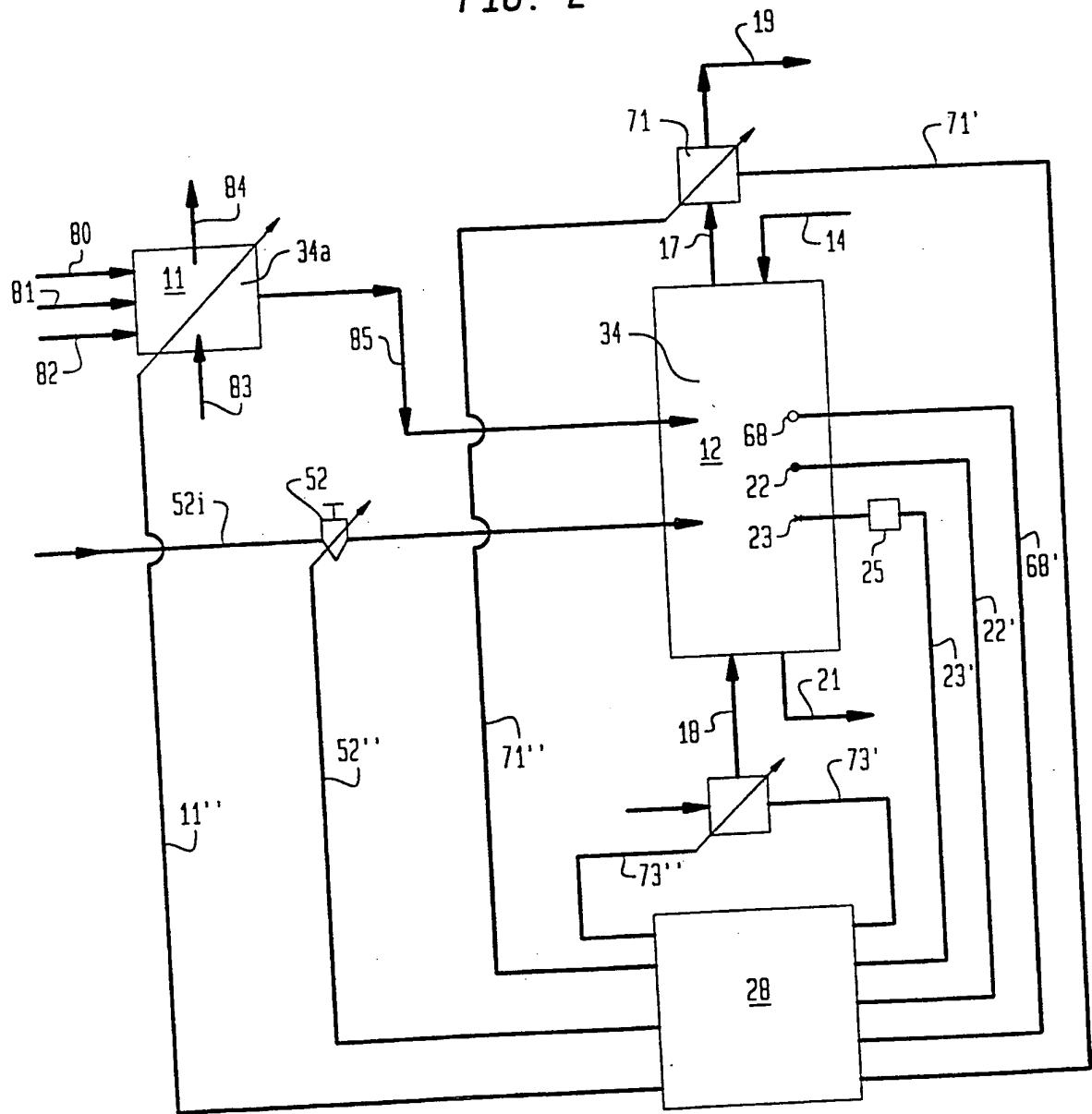
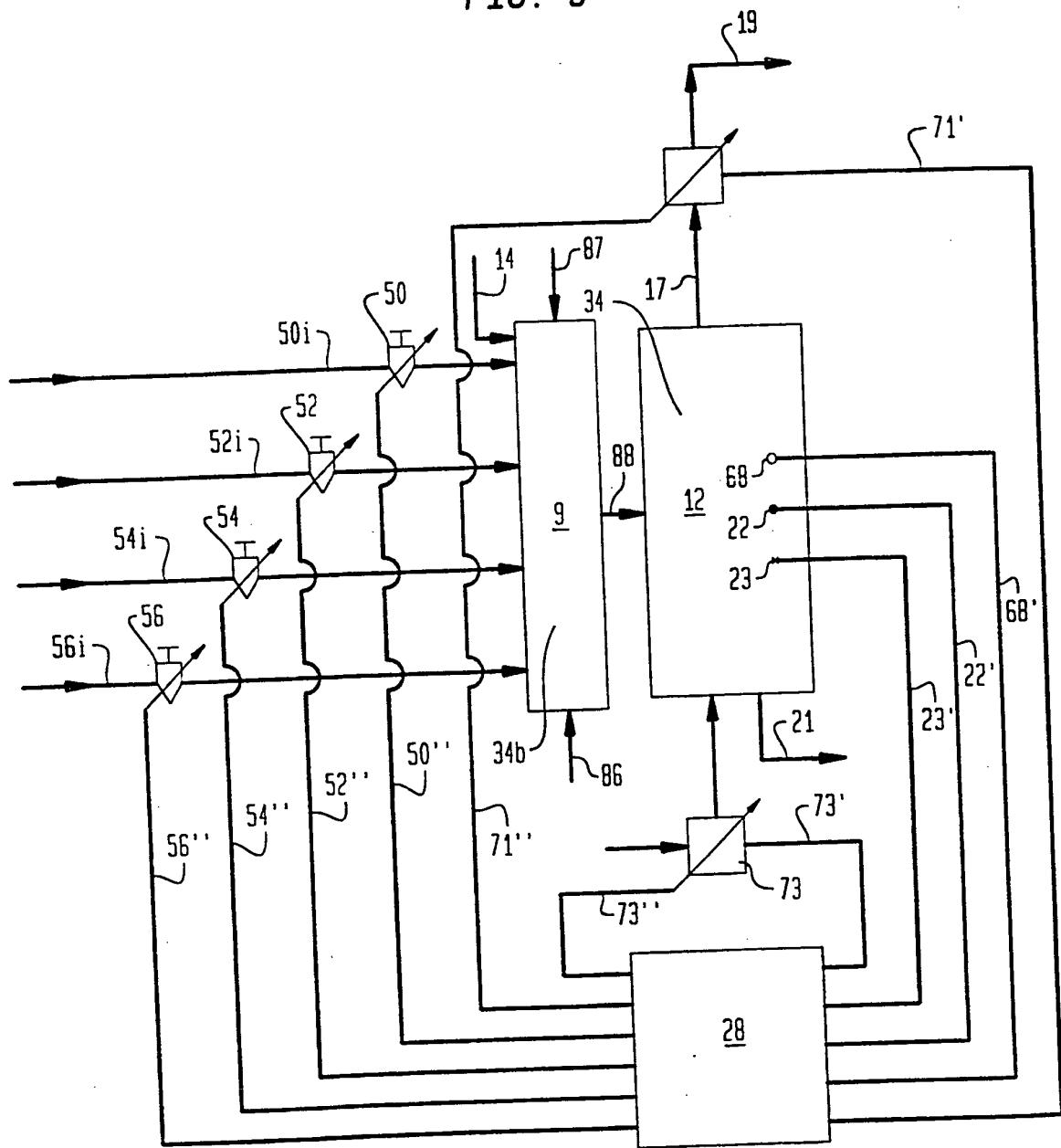


FIG. 2



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FIG. 3



INTERNATIONAL SEARCH REPORT

Int'l. Application No

PCT/US 97/17684

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 B01J19/00 C07C51/31 B01J19/26 B01J10/00

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 332 590 A (SMITH DEXTER E) 1 June 1982 see abstract; claim 1 see column 1, line 35 - line 37 see column 2, line 39 - line 42 see column 3, line 37 - line 51 see column 9, line 8 - line 11 see column 10, line 5 - line 22 --- EP 0 729 085 A (PHILLIPS PETROLEUM CO) 28 August 1996 see abstract; claim 1 see column 1, line 27 - line 36 see column 2, line 13 - line 20 see column 3, line 11 - line 20 see column 4, line 47 - line 58 see column 5, line 46 - line 59 see column 6, line 34 - line 49 --- -/-	1,5,13
A		1,13

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search

Date of mailing of the international search report

3 February 1998

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Name and mailing address of the ISA
 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040. Tx. 31 651 epo nl.
 Fax: (+31-70) 340-3016

Authorized officer

Lapeyrere, J

INTERNATIONAL SEARCH REPORT

National Application No

PCT/US 97/17684

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 729 084 A (PHILLIPS PETROLEUM CO) 28 August 1996 see abstract; claim 1 see column 2, line 20 - line 55 see column 4, line 40 - line 55 -----	1, 13
P, A	WO 96 40610 A (TWENTY FIRST CENTURY RESEARCH) 19 December 1996 see the whole document -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

PCT/US 97/17684

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4332590 A	01-06-82	NONE	
EP 0729085 A	28-08-96	US 5586051 A AU 673649 A CA 2164752 A CN 1133447 A CZ 9600555 A FI 960824 A JP 8245466 A NO 960745 A SG 38915 A	17-12-96 14-11-96 25-08-96 16-10-96 12-02-97 25-08-96 24-09-96 26-08-96 17-04-97
EP 0729084 A	28-08-96	US 5671153 A AU 677926 B AU 4094796 A CA 2161918 A CN 1135934 A CZ 9600556 A FI 960825 A JP 9104649 A NO 960746 A SK 24096 A	23-09-97 08-05-97 05-09-96 25-08-96 20-11-96 12-03-97 25-08-96 22-04-97 26-08-96 06-08-97
WO 9640610 A	19-12-96	US 5558842 A US 5580531 A US 5654475 A AU 5752296 A	24-09-96 03-12-96 05-08-97 30-12-96